ABSORPTION OF NO_2 INTO WATER AND NITRIC ACID SOLUTIONS IN A FIXED COLUMN

Abbas H. Sulaymon, Nahidh W. Kaseer* and Moneeb Khodhier Abbas
Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq
*Chemical Engineering Faculty - Military Collage of Engineering - Iraq

ABSTRACT

This study was directed to estimate the absorption rate of the equilibrium mixture of NO_2 / N_2O_4 *into water and dilute nitric acid solutions in a mixed column of packed bed and two sieve trays. The absorption rate was studied for liquid temperature (10–50 °C), liquid concentration (0-20 wt%*HNO_3*), liquid flow rate (40–200 l/h) and* NO_2/N_2O_4 *partial pressures (0.01–0.1atm). Measuring the liquid phase nitric acid concentration using two different techniques, acid–base titration and UV-spectroscopy, determined the absorption rates.*

The results confirm the hypotheses of chemical reactions in the liquid phase is the controlling factor in the process and N_2O_4 *rather than* NO_2 *dissolves and reacts with water. Also, it was found that the liquid flow rates have a slight influence on the absorption rates, which indicate faster reaction kinetics between* N_2O_4 *and water.*

Values of $HN_2O_4(kD_{N2O4,\,l})^{1/2}$ *were calculated. It had been found that the calculated values are in good agreements with the published data*

INTRODUCTION

Tail gases from plants that manufacture nitric acid constitute a source atmospheric pollution of considerable importance. In addition, the loss of nitrogen oxides (NO_x) obviously reduces the efficiency of the production plant and causes some economic damage [Kameoka and Pigford, 1977]. Meanwhile, because of the worldwide demands for environmental protection, the NO_x concentration in the waste gas has to be reduced. Therefore, more sophisticated calculation methods for studying and designing the absorption step of nitric acid process are being developed [Weisweiler et al, 1990]. The NO_x have two deleterious effects: they are responsible for the formation of "smog" and exert a direct toxic influence on human health [Weisweiler and Deib, 1981].

The absorption of NO_2 is the third step of producing nitric acid according to Ostwald process after two step oxidation of ammonia finally leading to NO_2 [Chilton, 1968]. Several control techniques have been demonstrated that reduce NO_x emissions from absorption columns in nitric acid manufacturing plants. Of the available control techniques, three methods are used predominantly, these are extended absorption, non-selective catalytic reduction and selective catalytic reduction [EPA, 1991]. It is important for absorption equipment to provide adequate gas-liquid contacting surface, sufficient gas phase residence time for the oxidation of NO to the more soluble NO_2^* ($NO_2+2N_2O_4$), and relatively low column temperatures to facilitate absorption and oxidation reactions [Counce and Perona, 1979].

It appears that the transfer of NO_2 or N2O4 from an inert carrier gas to water or diluted nitric acid can be explained by diffusional transfer of the equilibrium mixture of $NO_2 - N_2O_4$ (chemical equilibrium is very rapidly attained) in the gas phase followed by preferential dissolution and diffusional transfer of N_2O_4 in the aqueous phase combined with a fairly rapid first order reaction between N_2O_4 and water forming nitric and nitrous acids. The nitrous acid formed is decomposes to nitric acid, water and nitric oxide [Kramers et al, 1961].

In this study, measurements for the absorption rate of the equilibrium mixture NO_2/N2O4 in water and nitric acid solutions over a range of experimental conditions (liquid temperature, liquid concentration, liquid flow rate, and partial pressure of NO_2 in the gaseous mixture) are performed. These experiments are carried out in mixed column absorber that consists of packed bed and two sieve trays.

Mechanism of the Chemical Reactions

The chemical reactions involved in the steady state absorption of NO2 into water and dilute nitric acid appear to be adequately represented as follows:

$$2NO_2\,(g) \rightleftharpoons N_2O_4\,(g) \qquad (1)$$

$$N_2O_4\,(g) \rightleftharpoons N_2O_4\,(l) \qquad (2)$$

$$N_2O_4(l) + H_2O(l) \longrightarrow HNO_3(l) + HNO_2(l) \qquad (3)$$

$$3HNO_2(l) \longrightarrow HNO_3(l) + H_2O(l) + 2NO(g) \qquad (4)$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \qquad (5)$$

where (g) and (l) indicate gas and liquid species, respectively. A review of the literature indicates that the following assumptions relative to the overall reactions may be made.

1. NO_2 and N_2O_4 are in continuous gas phase equilibrium [Nonhebel, 1972; Verhoek and Daniels, 1931].
2. Reaction of N_2O_4 and water proceeds by means of a fast pseudo-first-order liquid phase reaction [Andrews and Hanson, 1961; Carberry, 1959; Caudle and Denbigh, 1953; Dekker et al, 1959; Kramers et al, 1961, Weisweiler and Deib, 1981; Weisweiler et al, 1990]. For NO_2* partial pressures > 0.01 atm, this is the predominant absorption reaction [Andrews and Hanson, 1961].
3. Liquid HNO_2 decomposes by eq.(4) [Lefers and Berg, 1982; Komiyama and Inoue, 1978].
4. Oxidation of gaseous NO occurs as an overall third-order gas phase reaction [Treacy and Daniels, 1955; Sherwood et al, 1975].

EXPERIMENTAL WORK

The experiments are carried out into a laboratory scale apparatus containing two sections, the generating section and the absorption section. The generating section mainly consists of reaction chamber, dehumidifier, two coolers, gas flow meters, and homogenizing chamber. Whilst, the absorption section consists of absorption column, liquid vessel, water bath, pump, and liquid flow meter. It is schematically shown in Fig. (1)

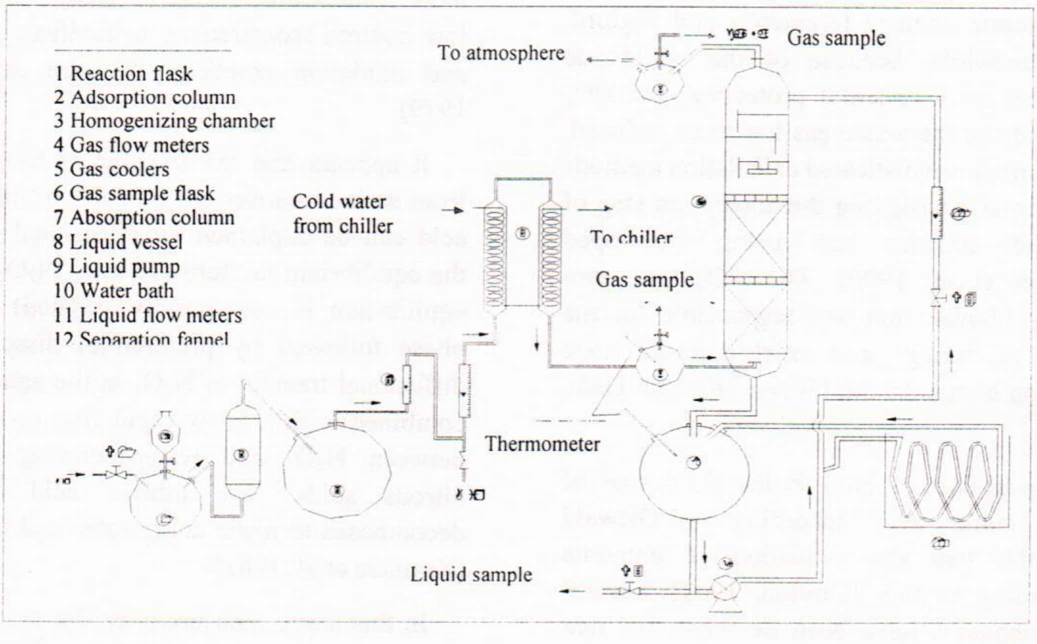

Fig. (1) The schematic diagram of the experimental apparatus

NO2 gas was generated in the reaction chamber by reacting pure copper with 98-wt % nitric acid according to the following equation [Chilton, 1968].

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g) + heat$$

To purify the generated gas (NO_2), the outlet line was incorporated with trap and dehumidifier column that was filled with silica gel. The temperature of the influent stream to the absorber section was maintained at constant temperature (25°C) by means of the two coolers. Prior to entering the absorber section, the inlet stream was diluted with air to a predetermined NO_2 partial pressure.

To justify the composition of the NO_2 in the inlet and outlet streams from the absorber, two round bottom flasks of 0.5-liter capacity are installed. These flasks are placed directly before and after the absorber.

The absorption of NO_2 will proceed by circulating nitric acid solution through the absorption column that consists of two sieve trays and packing medium. The column was constructed from Q.V.F. of 7.6 cm inside diameter and 120 cm height. The lower part of this column was packed with glass packing of Raschig ring type, whereas the upper part consisted of two sieve trays that were located directly above the packing. The column has the following design specifications that relevant to the used flow rates of gas (510 l/h) and liquid (40–200 l/h) to give a satisfactory hydraulic performance (i.e., no flooding in the packing and no weeping or jetting in the sieve trays)

i) Packed Bed : Material of packing is glass, type of packing is Raschig ring, bed high =0.8 m., nominal size of packing = 0.006 m., thickness of packing = 0.001 m., specific dry surface area = 289.33 m^2/m^3, fractional voidage of the bed = 0.876.

ii) Sieve – Trays: Material of the tray and down comer is plastic, down comer area = 12% of column area ،number of holes = 9, diameter of hole0.003 - m., hole pitch = 1.5 cm ،.weir height = 0.005 m., tray spacing = 0.15 m .

The Experimental work follows the following preparatory steps to establish steady operating conditions

1. Weighing different amounts of copper that determined by theoretical calculations of NO_2 partial pressures and placing it into the reaction flask.
2. Preparing five liters of nitric acid solution and transferring it into the liquid vessel after closing valve V_3.
3. Adjusting the temperature of the water bath to the ascribed liquid temperature.
4. Closing valve V_4 and switching on the pump. Nitric acid solution will be circulated between the storage vessel and the water bath. This process was carried out until the operating temperature of nitric acid solution was attained.
5. Opening valve V_4, the nitric acid would pass across the rotameter to the absorber column. The flow will continue till the temperature of the flowing liquid was adjusted at the required temperature.
6. Closing valve V_2 and opening valve V_1 will admit the airflow to the reaction flask. Different airflow rates are required to attain different NO2 partial pressures. Later on additional airflow from a side stream was added to the main airline to attain the desired value of gaseous mixture flow rate of the absorption column (8.5 l/min).

Till now the absorber was maintain through preparatory steps to attain steady conditions. Thereafter, dropping concentrated nitric acid from the separating funnel will generate the NO_2 and the experiment was begun.

At least three gas samples were withdrawn to analyze the composition of NO_2 in the gaseous mixture and average value was considered. To monitor the variation in nitric acid concentration through run duration two samples were withdrawn from nitric acid reservoir. These samples are withdrawn from valve V3. One sample is taken prior the beginning of the experiment and the second after the experiment was ended.

The experiment was terminated when faint color of NO_2 was noticed. Practically, the partial pressure of NO_2 in the gaseous mixture was experienced experimentally that already depending on the amount of copper in the reaction vessel, airflow rate from valve V1, and the flow rate of the concentrated nitric acid from the separating funnel.

The gas samples were taken by a gas bulb (conical flask of 250 ml capacity) that contained 20 ml of 10 vol.% hydrogen peroxide (H_2O_2) that readily absorbed NO_2. The bulb was fitted with self–sealing rubber stoppers and hypodermic needle valve was used to evacuate the bulb and introduce the gas sample.

The concentration of nitric acid that was generated from the reaction between H2O2 and NO_2-N_2O_4,as given by the following equation [Streuli and Averell, 1970]:

$$2NO_2+H_2O_2 \longrightarrow 2HNO_3 \qquad (7)$$

was determined by titration the contents of the gas bulb with 0.01 N NaOH solution

As shown by eq.(7) the number of moles of reacted NO_2 is equal to number of moles of nitric acid produced in the reaction. Assuming an ideal gas behavior for the gaseous mixture, the partial pressure of NO_2* could be calculated from ideal gas law, as follows:

$$P_{NO3} = \frac{n_{NO2}RT}{V_s} \qquad (8)$$

Vs were found by weighing an air sample.

The concentration of nitric acid was determined by titration with 1N NaOH and phenolphthalein indicator .For manipulating the experimentation of this work in accurate precision, the nitric acid concentrations was monitored by adapting Ultraviolet Spectrophotometer (Type, Shimadzu UV–206A, Japan) at absorption spectrum λmax equal to 303 nm [Komiyama and Inoue, 1978].

The absorption rate of N_2O_4 was calculated from the resulting nitric acid concentration by using the following expression [Kramers et al, 1961; Weisweiler and Dieb, 1981]:

$$N_{N_2O_4} = \frac{\left(\frac{3}{4}\right) * \Delta C_{HNO3} * V}{a_m * t} \qquad (9)$$

am is The specific interfacial area for mass transfer with respect to the packing and the two sieve trays, which calculated from dimensionless empirical correlation.

RESULTS AND DISCUSSION

Table (1) gives the calculated N2O4 absorption rate according to eq.(9) for different experiments

Table (1) Experimental results of the produced HNO3 concentration and the calculated N2O4 absorption rates for some experiments.

Table (1) Experimental results of the produced HNO3 concentration and the calculated N2O4 absorption rates for some experiments.

Run	Values of the Variable				ΔC_{HNO3} (kmol/m)	$N_{N2O4}*10^6$ (kmol/m^{2}sec)
	T (°C)	C_{HNO3} (wt.%)	L(l/h)	P_{NO2} (atm)		
2	20	15	160	0.0775	0.2290	3.931
3	40	5	160	0.0775	0.2898	4.912
5	40	15	160	0.0325	0.117	1.877
6	20	5	80	0.0325	0.1273	2.635
7	40	5	80	0.0325	0.1173	2.370
9	20	5	160	0.0325	0.1682	2.914
10	20	5	80	0.0775	0.2526	5.226
11	40	15	80	0.0325	0.0252	0.503
12	40	5	160	0.0325	0.1591	2.698
14	20	5	160	0.0775	0.3331	5.770
16	20	15	160	0.0325	0.1231	2.112
17	50	10	120	0.055	0.1377	2.469
18	30	20	120	0.055	0.0886	1.594
19	30	10	200	0.055	0.1937	3.138
20	30	10	120	0.100	0.2975	5.444
21	10	10	120	0.055	0.1798	3.371
22	30	0	120	0.055	0.2314	4.276
23	30	10	40	0.055	0.1030	2.551
24	30	10	120	0.010	0.0420	0.769
27	30	10	120	0.055	0.1511	2.765

Effects of the Studied Variables

In Fig.(2), the absorption rate is decreased with increasing liquid temperature. Rising liquid temperature increases the reaction rate constant between N_2O_4 and H_2O, which lead to better absorption, but at the same time the process is retarded due to lowering of the gas solubility and displacement of equilibrium between NO_2 and N_2O_4 towards NO_2. Therefore, gas solubility is more dominant than reaction rate at lower temperature, but with rising temperature the reaction rate effect will converge to the solubility effect and no further effect of the temperature on the absorption rate could be detect (as seen from the flatten the curve).

Figure (3) emphasis the effect of liquid concentration (wt. % of HNO_3) on absorption rate. It shows that lower absorption rate was monitored with higher liquid concentration. This decrease action of liquid concentration on absorption rate is contributed to lower solubility of the gas in the liquid phase due to increasing ionic strength with increasing nitric acid concentration. Besides the existence of free water molecules become relatively small with increasing acid concentration that consequently lowers the reaction rate between N_2O_4 and H_2O. This explanation had come in good agreement with Nonhebel (1972) who clarifies that neither alkalinity nor acidity of the absorption solution but only ionic strength is important on the solubility of the gases.

In Fig (4), higher absorption rate was found with increasing partial pressures of NO_2 in the bulk of the gas, which is simply proportional to the average partial pressure of NO_2. This increased dependency of the absorption rate on the partial pressure of NO_2 in the bulk of the gas was consistent with concentration occurrence of N_2O_4 at the interface that means higher mass transfer across the interface and higher reaction rate in the liquid phase.

There was a small sensitivity towards the liquid flow rate to the absorption rates, which might indicate that the diffusional resistance is accompanied by a rapid reaction between NO_2 and/or N_2O_4 and water. This one had coincided with the explanation of Dekker et al (1958) and Kramers et al (1961).

No interaction was found between liquid temperature and liquid concentration. As shown in Fig.(5), it seems that the absorption rate shows decrease function with increasing the temperature whatever liquid flow rate was. At high temperature levels (40 and 50 °C) especially at highest limit of liquid flow rates (160 and 200 l/h), the trend show slight decrease. This slight decrease at highest levels of liquid flow rate and temperature would be attributed to comparable influences that might arise between lower solubility, that might be accompanied with higher levels of liquid temperatures, and the increase action of liquid flow rates in the absorption rate of the transport species that was accompanied with lower diffusional resistance.

Figure (6) shows the significant interaction effect between liquid concentration and liquid flow rate. This significance was observed with monitoring the influential effect of liquid concentration on the absorption rate at each low rate. It seems that at low liquid concentration, higher absorption rate was noticed with lower liquid flow rate. This may attribute to unimportant diffusional resistance that is accompanied by a rapid reaction between NO_2 and/or N_2O_4 and water. In contrast, at higher liquid concentration (low free water molecules), absorption rates were higher observed with higher liquid flow rate. At high ionic strength, the decrease in absorption rates with higher liquid flow rate was accompanied by important diffusional resistance accompanied by slow reaction.

Figure (7) represent the interaction between liquid concentration and NO_2 partial pressure in the bulk of the gas. Insignificant interaction was observed between these two parameters. Although they tend to affect the absorption rate in opposite direction but still the NO2 partial pressure has the most important significance on absorption rate in comparison with liquid concentration. Meanwhile, the effect of NO_2 partial pressure was predominant in interaction with the other variables (liquid temperature and flow rate).

Theoretical Treatment

If $NO_2 - N_2O_4$ gas mixture are absorbed from a carrier gas stream, both are transferred from the gas phase to the gas–liquid interface. Across the interface (in the liquid side from the interface) in addition to diffusion, a pseudo first order chemical reaction occurs between N2O4 and H2O. At steady state condition, this diffusion

$$D_{N2O4,l}\frac{d^2C_{N2O4}}{dx^2} - k\,C_{N2O4} = 0 \qquad \text{....(10)}$$

accompanying the reaction which can be described by the following differential equation

with the boundary conditions :

i) for $x = 0 \qquad C_{N2O4} = C^{i}_{N2O4} \qquad (11)$

ii) for $x = \delta l \qquad C_{N2O4} = C^{o}_{N2O4} \qquad (12)$

Solving the above equation and taking into account Hatta number ،

$$H_a = \delta_l \qquad (k/D_{N2O4,l})^{1/2} \qquad (13)$$

And applying, $k_{l,\,N2O4} = D_{N2O4,l}\,(\delta_l)^{-1} \qquad (14)$

An equation for the mass transfer rate is established [Weisweiler et al, 1990]:

$$N_{N_2O_4} = \frac{H_a}{\tanh(H_a)}\left[1 - \frac{C_{N_2O_4}}{C^{i}_{N_2O_4}}\frac{1}{Cosh(H_a)}\right]K_{1,N_2O_4}C^{i}_{N_2O_4} \quad (15)$$

For a fast chemical reaction, eq.(15) can be simplified to [Sherwood et al, 1975; Weisweiler et al, 1990]:

$$N_{N_2O_4} = (kD_{N_2O_4,1})^{1/2}C^{i}_{N_2O_4} \qquad (16)$$

The equilibrium at the gas–liquid interface, as a condition in the two film theory, can berepresented by Henrys law,

$$C^{i}_{N_2O_4} = H_{N_2O_4}\,P^{i}_{N_2O_4} \qquad (17)$$

Incorporating the above expression to eq.(16), the two film theory of mass transfer accompanied by a rapid pseudo first–order reaction in the liquid could be expressed the absorption rate by the following equation:

$$N_{N_2O_4} = H_{N_2O_4} (k D_{N_2O_4,l})^{1/2} P^i_{N_2O_4} \tag{18}$$

The mass transfer rate for the simultaneous diffusion of NO_2 and N_2O_4 through a stagnant as film, on the bases of the two film theory, at steady state condition is equated to the reaction rate in the liquid phase and , therefor, to the absorption rate. This rate can be calculated by the following equation : [Wendel and Pigford, 1958; Nonhebel, 1972]:

$$N_{N_2O_4} = \frac{k_{gNO_2}}{2RT}\left[P^o_{NO_2} - P^i_{NO_2}\right] + \frac{k_{gN_2O_4}}{RT}\left[P^o_{N_4O_2} - P^i_{N_4O_2}\right] \tag{19}$$

The equilibrium composition of NO_2-N_2O_4 gas mixture is strongly depends on temperature. The temperature dependence of the equilibrium constant is given by Verhock and Daniels (1931), as follows:

$$\log\ Kp = \frac{3193}{T} - 9.8696 \tag{20}$$

Where Kp is the equilibrium constant defined as:

$$Kp = \frac{P_{N2O4}}{P^2_{NO2}} \tag{21}$$

Incorporating eq.(21) to eq.(19) gives:

$$N_{N2O4} = \frac{k_{gNO_2}}{2RT(K_P)^{1/2}}\left[\left(P^o_{N_4O_2}\right)^{1/2} - \left(P^i_{N_4O_2}\right)^{1/2}\right] + \frac{k_{gN_2O_4}}{RT}\left[P^o_{N_4O_2} - P^i_{N_4O_2}\right] \tag{22}$$

Hence, interfacial partial pressure of N_2O_4 can be calculated from eqs (9) and (22). Gas phase mass transfer coefficiente for NO_2 and N_2O_4 was obtaind from a dimensionless emperical correlation given by Norman (1961) that holds for packed bed only, as follows:

Bulk N_2O_4 partial pressure is taken as the arithmetic mean of inlet and outlet N_2O_4 partial

$$\frac{k_{gi}.d_p}{D_i} = 3.0\left(\frac{U_g.D_c.\rho_g}{\mu_g}\right)^{0.8}\left(\frac{\mu_g}{\rho_g.D_i}\right)^{1/3}\left(\frac{d_p}{H}\right) \tag{23}$$

pressures, which calculated from the measured inlet and outlet NO_2^* partial pressures, where

$$P^*_{NO_2} = P_{NO_2} + 2P_{N_2O_4} \tag{24}$$

Substituting eq (2.15) in eq (4.12) gives:

$$P_{NO_2^*} = \frac{1}{(K_p)^{1/2}}\left(P_{N_2O_4}\right)^{1/2} + 2P_{N_2O_4} \tag{25}$$

Figure (8) gave a sample of the relation between N2O4 absorption rate and N_2O_4 interfacial pressure at $CHNO_3$ = 10 wt% and L = 40 l/h.

According to eq (18), plotting N_2O_4 absorption rate versus P^i_{N2O4} will give a straight line with a slop equal to H_{N2O4} (k $D_{N2O4,l})^{1/2}$. These five figures give good straight lines passing near the origin point. That confirms the hypothesis of N2O4 is the reacting and transporting species into the liquid phase.

Values of H_{N2O4}(k $D_{N2O4,l})^{1/2}$ calculated in the present work are listed in Table (2) . Values of H_{N2O4}(k $D_{N2O4,l})^{1/2}$ calculated by several investigators using different laboratory absorbers (contactors) are represented in Table (4) as well as the calculated values of the present work. Figure (9) shows the calculated values of H_{N2O4} $(kD_{N2O4,l})^{1/2}$ as a function of temperature for the used liquid concentrations.

Table (2) Values of $H_{N2O4}(kD_{N2O4,\ l})^{1/2}$ $*10^3$ {kmol/m^2sec.atm} obtained in the present work as a function of liquid concentration and temperature.

C_{HNO3} (wt%)	Temperature of Absorption (°C)				
	10	20	30	40	50
0	1.382	1.076	0.930	0.839	0.826
5	0.933	0.716	0.611	0.543	0.535
10	0.731	0.499	0.404	0.341	0.329
15	0.530	0.40	0.311	0.274	0.262
20	0.421	0.318	0.253	0.240	0.231

Table (3) Values of $H_{N2O4}(kD_{N2O4,l})^{1/2}$ of the present work and those published by other investigators

Reference	C_{HNO3} (wt %)	Temperature (°C)	$H(kD_l)^{1/2}$ $10^{3}\cdot$ (kmol/m²s.atm)	Contact Pattern
Wendel and Pigford (1958)	0	25	0.5774	Wetted wall column
	0	40	0.537	
Dekker *et al* (1959)	0	25	1.114	Wetted wall column
	0	35	1.003	
Kramers *et al* (1961)	0	20	0.77	Jet absorber
	0	30	0.891	
Kameoka and Pigford (1977)	0	25	0.685	Wetted sphere absorber
Weisweiler and Deib (1981)	0	25	0.486	Falling film absorber
Lefers and Berg (1982)	25	20	0.496	Wetted wall column
	40	20	0.182	
Miller (1987)	67	30.3	1.562	Bubble cap plate column
	28.5	38.5	1.903	
	8.5	37.5	2.411	
	58	30.8	0.826	Sieve plate column
	39.4	33.2	0.871	
	18.1	32.9	1.464	
	11.0	30.6	2.411	
Weisweiler *et al* (1990)	15	25	0.476	Double stirrer cell
	15	35	1.394	
	45	25	0.105	
	45	35	0.333	
	60	25	0.018	
Kaseer(2000)	0	20	0.58	Double stirrer absorber
	10	20	0.44	
	20	20	0.34	
Kaseer *et al* (2000)	0	20	0.54	Flat surface absorber
	10	20	0.69	
	20	20	0.80	
This Work	0	10	1.38	Mixed Column
	0	30	0.93	
	0	50	0.826	
	10	10	0.731	
	10	30	0.404	
	10	50	0.329	
	20	10	0.421	
	20	30	0.253	
	20	50	0.231	

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The stronger dependence of absorption rate on NO_2 partial pressure in the gas phase relative to other variables indicates that the process is controlled by chemical reaction in the liquid phase.
2. The linear dependence of absorption rate with N_2O_4 interfacial partial pressure confirm the hypotheses of N_2O_4 is the reactive species of the $NO_2 - N_2O_4$ equilibrium mixture, which dissolves in the liquid and reacts with water according to a pseudo first order chemical reaction.
3. Gas solubility and reaction rates are the key factors that contribute to the liquid concentration and temperature dependence of the absorption rate of NO_2/N_2O_4 into water and dilute nitric acid. However, gas solubility shows pronounce effect than reaction rate at low temperature and concentration. Low effect on absorption rate was noticed with increasing the temperature of absorption.
4. Changing liquid flow rate cause a slight change in absorption rate. This confirms the hypothesis that no diffusional resistance was submitted from mass transfer. At lower concentration (0 wt% HNO_3) the absorption rate was slightly decreased by increasing the liquid flow rate. But, at higher concentration (20 wt % HNO_3) the absorption rate was slightly increased by increasing the liquid flow rate.

NOMENCLATURE

a_m : surface area for mass transfer of the packing and sieve trays (m^2/m^2)
C_j : concentration of species "j" ($kmol/m^3$)
C^i_{N2O4} : interfacial concentration of N_2O_4 ($kmol/m^3$)
C^o_j : bulk concentration of species "j" ($kmol/m^3$)
D_c : column diameter (m)
$D_{j,g}$: gas phase diffusivity of species "j" (m^2/s)
$D_{j,l}$: liquid phase diffusivity of species "j" (m^2/s)
d_p : packing diameter (m)
H : packed bed height (m)
H_{N2O4} : Henry constant of N_2O_4 ($kmol/m^3.atm$)
k: first order reaction rate constant for N_2O_4 hydrolysis (s^{-1})
$k_{g,j}$: gas phase mass transfer coefficient of species "j" (m/s)
$k_{l,j}$:liquid phase mass transfer coefficient of species "j" (m/s)
K_P: equilibrium constant of NO2/N2O4 gas mixture (atm-1)
L : liquid mass flow rate (l/h)
N_j : absorption rate of species "j" ($kmol/m^2.s$)
n_{NO2}* : moles of equilibrium mixture NO_2/N_2O_4 (kmol)
P : total pressure (Pa)
P_j : partial pressure of species "j" (atm)
P^i_j : interfacial partial pressure of species "j" (atm)
P^o_j : bulk partial pressure of species "j" (atm)
R : gas constant ($atm.m^3/kmol.°K$)
T : temperature (°K)
t : time (s)
U_g : gas velocity (m/s)
V : volume of the circulating liquid (m^3)
V_s : volume of gas sample (m^3)
ρ_g : gas density (kg/m^3)
μ_g : gas viscosity (Pa.s)
λ_{max} : maximum wave length (nm)
δ_l : liquid film thickness (m)

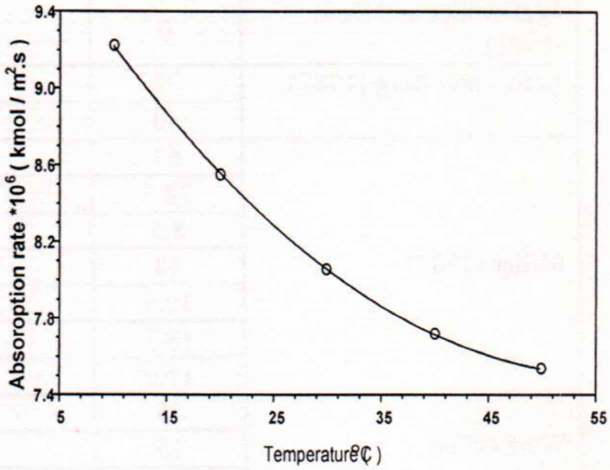

Fig (2) Absorption rate as a function of liquid temperature

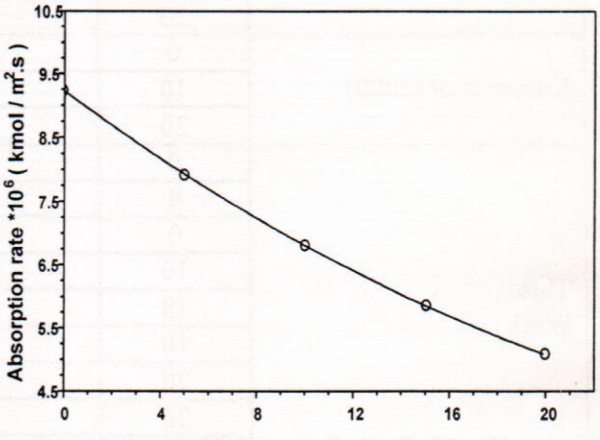

Fig (3) Absorption rate as a function of liquid concentration

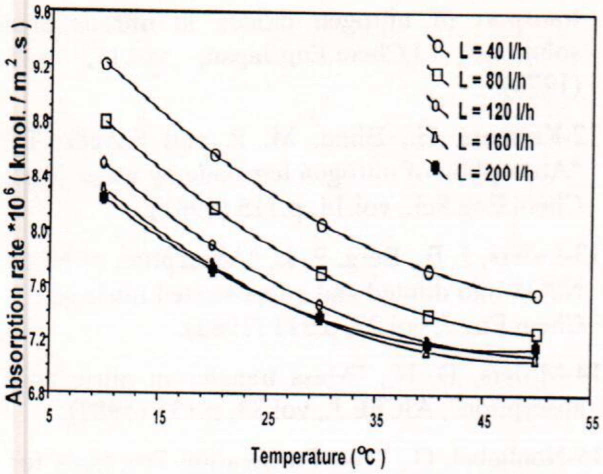

Fig (4) Absorption rate as a function of NO_2 partial pressure

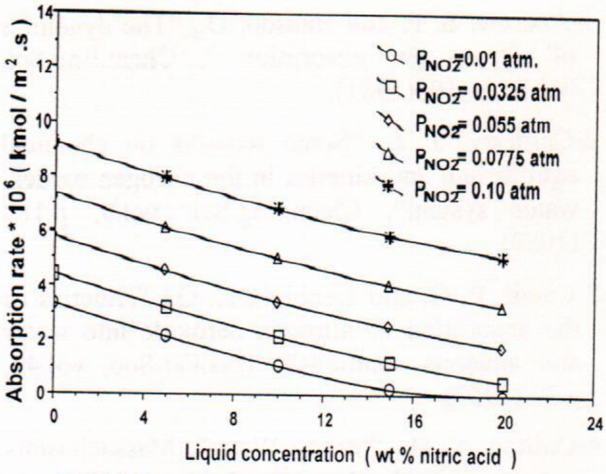

Fig (7) Absorption rate as a function of liquid concentration and NO_2 partial pressure

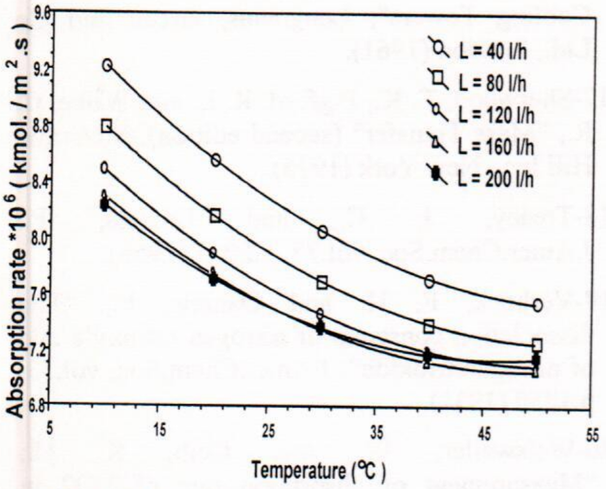

Fig (5) Absorption rate as a function of liquid temperature and liquid flow rates

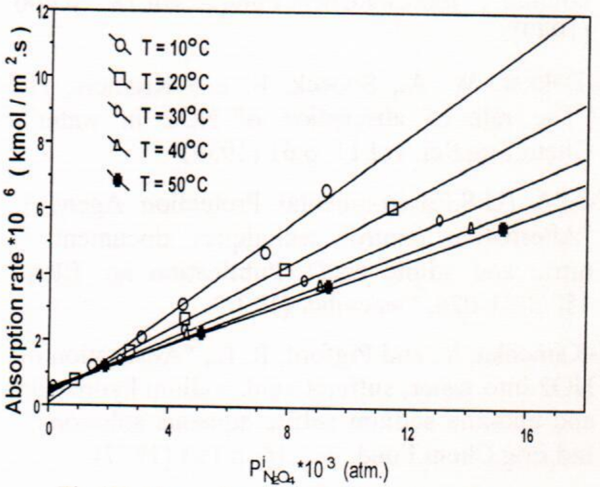

Fig (8) Absorption rate as a function of N_2O_4 interfacial partial pressure at 10 wt % HNO_3 and various temperatures

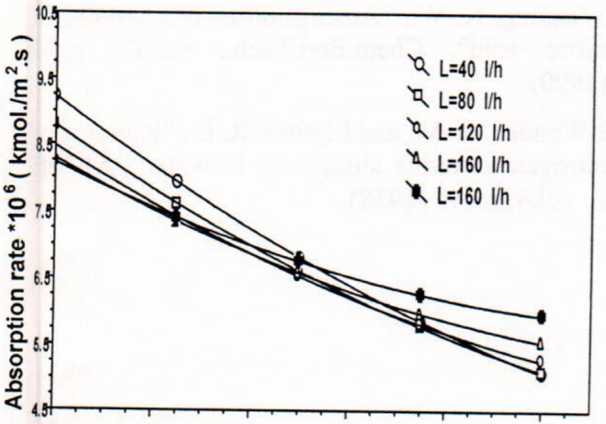

Fig (6) Absorption rate as a function of liquid concentration and liquid flow rates

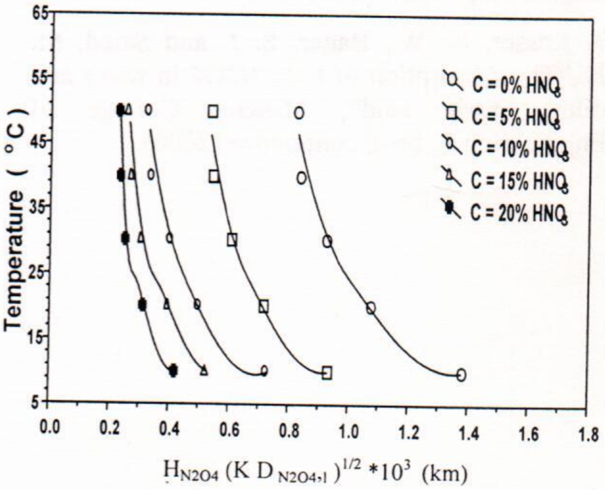

Fig (9) Calculated values of $H_{N2O4}(kD_{N2O4,\ l})^{1/2}$ as a function of temperature at different liquid concentrations

REFERENCES

1-Andrew, S. P. and Hanson, D., "The dynamics of nitrous gas absorption ", Chem.Eng.Sci, vol.14, p. 105(1961).

2-Carberry, J .J., "Some remarks on chemical equilibrium and kinetics in the nitrogen oxides-water system", Chem.Eng.Sci, vol.9, p.189 (1959).

3-Caudl, P. G. and Denbigh, K. G., "Kinetics of the absorption of nitrogen peroxide into water and aqueous solutions", Tras.Far.Soc, vol.49, p.39 (1953).

4-Chilton, T. H., "Strong Water", Massachusetts Institute of Technology, Cambridge (1968).

5-Counce, R. M. and Perona, J. J., "Gaseous nitrogen oxide absorption in a sieve plate column", Ind.Eng.Chem.Fund., vol.18, p.400 (1979).

6-Dekker, W. A., Snoeck, E. and Kramers, H., "The rate of absorption of NO2 in water", Chem.Eng.Sci, vol.11, p.61 (1959)

7-EPA (U.S.Environmental Protection Agency), "Alternative control techniques document – nitric and adipic acid", Publication no. EPA-450/3-91-026, December (1991).

8-Kameoka, Y. and Pigford, R. L., "Absorption of NO2 into water, sulfuric acid, sodium hydroxide and alkaline sodium sulfite aqueous solutions", Ind.Eng.Chem.Fund., vol.16, p.153 (1977).

9-Kasser, N. W., "Absorption of NO2/N2O4 in water and dilute nitric acid in a stirrer absorber", Iraqi Journal of Chemical and Petroleum Engineering, vol.1, p.67 (2000).

10- Kasser, N. W., Baqer, S. J. and Saied, M. H.,"The Absorption of NO2/N2O4 in water and dilute nitric acid", Military College of Engineering J., third conference (2000).

11-Komiyama, H. and Inoue, H., "Reaction and transport of nitrogen oxides in nitrous acid solutions", J.Chem.Eng.Japan, vol.11, p.15 (1978).

12-Kramers, H., Blind, M. P. and Snoeck, E., "Absorption of nitrogen tetroxide by water jets", Chem.Eng.Sci., vol.14, p.115 (1961).

13-Lefers, J. B., Berg, P. J., "Absorption of NO2-N2O4 into diluted and concentrated nitric acid", Chem.Eng.J, vol.23, p.211 (1982).

14-Millers, D. N., "Mass transfer in nitric acid absorption", AIChE J., vol.33, p.135 (1987).

15-Nonhebel, G., "Gas Purification Processes for Air Pollution Control", Newnes – Butterworths, London (1972).

16-Norman, W. S., "Absorption, Distillation and Cooling Towers", Longmans, Green and Co Ltd., London (1961).

17-Sherwood, T. K., Pigford, R. L. and Wilke, C. R., "Mass Transfer" (second edition), McGraw-Hill Inc., New York (1975).

18-Treacy, J. C. and Daniels, F., J.Amer.Chem.Soc, vol.77, p.2033 (1955).

19-Verhock, F. H. and Daniels, F., "The dissociation constants of nitrogen tetroxide and of nitrogen trioxide", J.Amer.Chem.Soc, vol.53, p.1250 (1931).

20-Weisweiler, W. and Deib, K. H., "Measurement of absorption rate of NO2 in water in a falling film absorber", Ger.Chem.Eng., vol.4, p.79 (1981).

21-Weisweiler, W., Eidam, K., Thiemann, M. and Wiegang, K. W., "Absorption of NO2-N2O4 in nitric acid", Chem.Eng.Tech., vol.13, p.97 (1990).

22-Wendel, M. M. and Pigford, R. L., "Kinetics of nitrogen tetroxide absorption in water", AIChE J., vol.4, p.249 (1958).